COATINGS. ENAMELS

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EFFICIENCY OF DEPOSITING GLASS ENAMELS BY ELECTROPHORESIS

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The factors affecting the efficiency of depositing glass enamel by electrophoresis is considered. It is established that the densest and most uniform coating are obtained on steel samples with preliminary deposited nickel. An optimum composition of slip is obtained and the conditions of depositing glass coating by electrophoresis is determined.

The application of one-coat enameling is becoming increasingly topical in view of the constantly growing cost of power and material resources. One-coat enamel combines the properties of the undercoat and surface layers, i.e., the protective and decorative properties [1].

The quality of metal that is to be coated, the technology of its surface preparation, the composition of enamel, and enameling conditions have great significance in one-coat enameling of steel. Metals used for single-coating enameling are usually titanium-bearing steel or decarbonized, low-carbon, and alloyed steels.

There are various methods for enamel deposition: moist, powder, electric-immersion, etc. The most common in enameling practice are the wet (slip) method and the dry method (powder deposition). Wet application is implemented by spraying (pulverizing), immersion, flow coating, or using a brush. Dry deposition can be either electrostatic, or application of powder to the article preheated to 500 – 600°C [2]. However, the specified methods have some disadvantages: poor technological efficiency, nonuniform thickness of coating, striping, and, as a consequence, deteriorated adhesion.

We investigated the electrophoretic method of depositing glass enamel coatings that has a number of advantages: low specific consumption of material and the possibility of achieving uniform density and low thickness in a coating.

The preliminary treatment of samples before applying coating was performed in accordance with recommendations in [3].

Initially the deposition of glass enamel coatings was performed using a low-concentration suspension (slip) of the composition (g/liter): 20 vitreous frit, 17 clay, 0.02 sodium chloride; 0.5 carbomethyl cellulose (CMC). The anode current density in precipitation varied within an interval from 0.5 to 0.9 A/dm^2.

According to published data [3], in electrophoretic deposition of coating, the strength of current in electrolysis decreases significantly, virtually to zero, which presumably occurs due to the electric insulation of the metal of the coating after the end of the process. In electrolyte suspension with a CMC additive the strength of current did not decrease in electrolysis and the coating was not precipitated. This is presumably related to the insufficient suspending capacity of CMC, which leads to the stratification of the slip with precipitation of the glass frit. Therefore, it is necessary to use materials that are more effective dispersing agents and to increase the concentration of glass frit in the slip.

In further experiments we attempted to replace CMC by sodium-potassium silicate solution (water glass). The chemical composition of water glass is as follows (%)[2]: 69.30 – 72.00 SiO_2, 7.50 – 9.20 K_2O, 18.40 – 20.70 Na_2O, 0.80 Fe_2O_3 and Al_2O_3, 0.25 CaO, 0.15 MgO, and 0.35 SO_2. The silica modulus of water glass is 2.75 – 3.10. A perceptible decrease in the strength of current was observed in electrolysis of the electrolyte suspension with a water glass additive. The experiments were performed with different values of initial current density — from 0.1 to 0.9 A/dm^2. It was found that within the current density range from 0.1 to 0.4 A/dm^2 the coating is not precipitated, whereas from 0.5 to 0.9 A/dm^2 the sample is fully covered by enamel.

As the strength of current varies in time, the effect of voltage on the external appearance and adhesion strength of the coating was investigated. The voltage varied from 8 to 14 V. The most homogeneous and strong coating were precipitated under the voltage of 10 and 12 V. In this case there

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[2] Here and elsewhere in wt.%.

is no intense release of oxygen on the electrode, therefore, the resulting coating is nonporous.

To obtain dense precipitates, it is advisable to use pulse current for enamel deposition [4]. This makes it possible to decrease specific energy consumption, increase the velocity of dispersed particles, and expand the possibilities of regulating the coating deposition conditions by varying the electric parameters. To estimate the efficiency of pulse current for electrophoretic coating application, we used current of the half-wave rectification of industrial frequency. The scheme of the plant for applying glass-enamel coatings is shown in Fig. 1.

Preliminary experiments indicated that when glass enamel is precipitated directly on steel, the steel substrate partially becomes electrochemically dissolved, which later, in drying the sample with the glass-enamel coating results in a significant modification of the coating color: from light blue to dark brown. To prevent these negative phenomena and to ensure sufficient strength of adhesion of steel to the coating and a good quality, the metal requires additional treatment. The most common method for preparing steel surface for enameling is electrolytic deposition of thin metallic films, since it has several advantages over other methods: a high degree of purity of electrolytically precipitated metal; high chemical resistance of metallic coating determined by the purity of the precipitate; low metal consumption; the possibility of a precise control of coating thickness; good mechanical properties of coating (elasticity, good adhesion to steel).

Since electrophoretic deposition of enamel coating is implemented in a weakly alkaline medium, nickel was selected for coating on steel, since is stays passive in an alkali medium [3]. The pretreatment of samples was performed as specified in Table 1.

After that a nickel layer 3 μm thick was electrolytically deposited on a steel sample. The composition of the electrolyte was as follows (g/liter): 10.0 NaCl, 295.0 $NiSO_4 \cdot 7H_2O$, 30.0 H_3BO_3, 0.5 1.4-butyndiol, and 2.5 chloramine B. The electrolyte temperature was 20 – 60°C, pH = 1.5. The solution was prepared by consecutively dissolving the reactants in water at a temperature of 40 – 60°C under constant stirring.

TABLE 1

Process	Solution composition, g/100 ml	Temperature, °C	Duration, min
Degreasing	4.0 Na_2CO_3 4.0 NaOH 0.3 water glass	100	6 – 10
Washing	Flow water	20 – 25	1 – 2
Pickling	11.0 HCl	20 – 25	6 – 10
Washing	Flow water	20 – 25	1 – 2
Neutralization	0.6 Na_2CO_3 0.3 Na_3PO_4	95 – 100	5
Drying	–	100	5

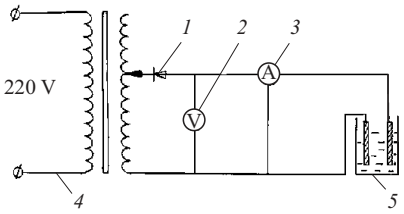

Fig. 1. Scheme of the plant for electrophoretic deposition of glass enamel coatings: *1*) diode, *2*) voltmeter; *3*) ampermeter; *4*) transformer; *5*) galvanic bath.

The thickness of nickel coating was selected based on preliminary studies, which established that the optimum thickness is 3 μm. With a lower thickness of nickel coating the slip penetrates through the pores to the steel substrate and causes corrosion of steel, consequently, the minimum thickness of the nickel coating should be 3 μm. A coating of a larger thickness is not cost-effective.

The duration of depositing the nickel coating was determined from the formula:

$$\tau = \frac{\delta\rho}{Y_c E_k i S},$$

where τ is the coating application duration, h; δ is the coating thickness, μm; ρ is the coating density g/cm^3; Y_c is the current yield, %; E_k is the electrochemical equivalent, g/(A · h); i is the current density, A/dm^2; S is the surface area of the sample, dm^2.

The cathode current density was taken in accordance with GOST 9.305–84.

After the electric precipitation of nickel, the slip of electrolyte suspension of the following composition (%): 35.0 frit, 57.0 water, 0.6 borax, 5.0 clay, and 2.4 water glass was deposited on samples with a surface area of 0.2 dm^2.

To identify the effect of the composition of electrolyte suspension and the conditions of electrolysis on the quality of coating, the Box – Willson method for a mathematical design of experiment was used [5]. Preliminary experiments demonstrated that the content of borax, clay, and water glass in electrolyte suspension has no perceptible effect on the quality of the coating, accordingly, on experiments they were taken to be constant. The conditions of designing a full three-factor factorial experiment are specified in Table 2 and

TABLE 2

Factor	C_{fr},* %	i, A/dm^2	τ, min
Code	x_1	x_2	x_3
Main level	35	3	3
Variation interval	5	1	1
Upper level	40	4	4
Lower level	30	2	2

* Content of frit in the slip.

TABLE 3

Experiment	Factor						Response function			
	coded values			true values						
	x_1	x_2	x_3	C_{fr}, %	i, A/dm^2	τ, min	y_1	y_2	y_3	y_s
1	–	–	–	30	2.0	2	3.0	3.2	3.3	3.16
2	–	–	+	30	2.0	4	1.2	1.3	1.5	1.33
3	–	+	+	30	4.0	4	1.5	1.5	1.3	1.43
4	+	+	+	40	4.0	4	3.5	3.4	3.5	3.46
5	+	–	–	40	2.0	2	4.8	4.6	5.0	4.80
6	+	+	–	40	4.0	2	1.9	2.4	2.3	2.20
7	–	+	–	30	4.0	2	0.7	0.4	0.5	0.53
8	+	–	+	40	2.0	4	1.3	1.6	1.5	1.46

TABLE 4

Grading	Estimate criteria		
	fusion, grade	adhesion strength, grade by GOST 244405–80	burn-outs, % of sample surface area
0	0 – 1	0 – 1	> 50
1	1 – 2	0 – 1	30 – 50
2	3 – 4	1 – 2	10 – 30
3	5 – 6	2 – 3	5 – 10
4	7 – 8	3 – 4	≤ 5
5	9 – 10	4 – 5	–

the design matrix and experimental results in Table 3. All experiments were repeated thrice. Firing of the samples was performed at 850°C.

The additives to the slip included (%): 0.6 borax, 4.9 clay, and 2.3 water glass.

The quality of the coating was estimated visually in accordance with the criteria specified in Table 4.

The most homogeneous, smooth coating without burnouts and with a strong adhesion was the coating with the following glass frit composition (%): 40.0 frit, 52.0 water, 0.6 borax, 4.9 clay, and 2.3 water glass. The current density was 2.0 A/dm^2, precipitation duration 2 min, and the surface area of the sample 0.2 dm^2.

The next operation was constructing the regression equation. As a result of calculations, the following equation was obtained:

$$y = 2.296 + 0.683x_1 - 0.391x_2 - 0.376x_3 + 0.241x_1x_2 - 0.143x_1x_3 + 0.916x_2x_3 .$$

Based on this regression, it was found that the maximum positive effect increasing the response function is observed from increasing the concentration of the frit in the slip. On the other hand, the current density and the duration of coating application ought to be decreased.

Thus, the performed research has identified the optimum composition of electrolyte suspension and the optimum conditions for coating deposition by electrophoresis, as well as the main factors influencing this process.

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